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Giant Nonlinear Optical Response of Interacting One-Dimensional Frenkel Excitons in Molecular Aggregates

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Experimental results for the nonlinear optical properties of thin films of molecular J-aggregates of substituted pseudoisocyanine (PIC) are reported. These molecular aggregates were found to possess a giant third-order optical nonlinearity ($|\chi^{(3)}| \approx 10^{-5}$ esu). Thin films of J-aggregates of PIC iodide with several different N-alkyl substituents were obtained to study the effect of disorder on the nonlinear optical properties. The spectral features of the nonlinear optical susceptibility are analyzed within a model that includes exciton–exciton interactions.

Introduction Recently, the optical dynamics of low-dimensional systems such as J-aggregates, Langmuir-Blodgett films, quantum wells, and conjugated polymers have drawn considerable attention. These systems allow one to investigate the changes between single particles and bulk solids. Moreover, the collective optical phenomena of such systems are of much interest. A well-known example of a collective optical phenomenon is the enhancement of the nonlinear optical properties. Previous experimental and theoretical works have shown that molecular J-aggregates are self-organized quasi-one-dimensional systems of cyanine dyes [1] that combine a strong third-order optical susceptibility in the exciton absorption band (J-band) ($|\chi^{(3)}| \approx 10^{-7}$ to 10^{-6} esu) [2 to 5] with a short response time ($\approx 10^{-12}$ s) [4, 6, 7]. The enhancement of the nonlinear optical properties results from the exciton delocalization over the aggregate [8]. As the exciton delocalization length is determined by the degree of order within the aggregates, disorder strongly influences the optical and nonlinear optical properties of the aggregates [9].

This work presents the results of an experimental study of linear and nonlinear optical properties of thin films of J-aggregates of PIC with several N-alkyl substituents. While these substituents do not modify the optical properties of an isolated molecule, they do affect the aggregate formation and, thereby, the degree of order.

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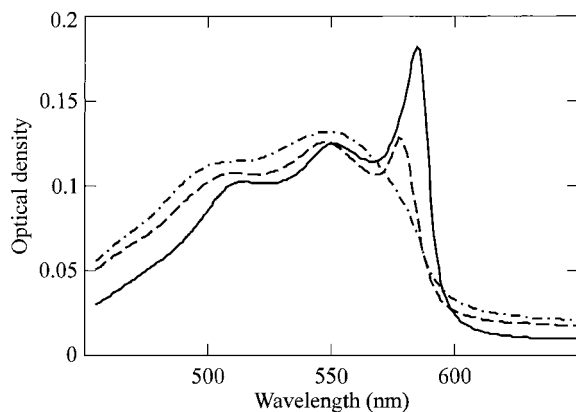


Fig. 1. Linear absorption spectra for films of J-aggregate of PIC with substituents $C_2H_5-C_{10}H_{21}$ (dot-dashed line), $C_2H_5-C_{15}H_{31}$ (dashed line), and $C_2H_5-C_{18}H_{37}$ (solid line). The films were obtained by spin-coating from dye solutions of acetonitrile at a concentration of $\approx 10^{-3}$ M with a spinning velocity of 3000 rpm

Experimental Results For the preparation of samples we have used PIC with N-alkyl substituents of different length: $C_2H_5-C_{10}H_{21}$, $C_2H_5-C_{15}H_{31}$, and $C_2H_5-C_{18}H_{37}$ [10]. Films of J-aggregates of these dyes with a thickness of 30 nm were obtained by spin-coating (at 1000 to 3000 rpm) on a glass substrate from dye solutions (acetonitrile or ethylene dichloride) at concentrations of $\approx 10^{-2}$ M. The film thickness was measured by spectral ellipsometry and atomic force microscopy.

Figure 1 shows the linear absorption spectra for samples obtained from dye solutions at a low dye concentration of $\approx 10^{-3}$ M. The band at 550 nm represents the monomer dye absorption and the band at 585 nm represents the exciton absorption band of the J-aggregates that have formed. We observe that with a growing length of the alkyl substituents, the tendency to form J-aggregates increases. As is seen in Fig. 1, PIC with $C_2H_5-C_{10}H_{21}$ hardly forms J-aggregates, while PIC with $C_2H_5-C_{15}H_{31}$ and $C_2H_5-C_{18}H_{37}$ do. Moreover, the value of the optical density at the J-band maximum for PIC with $C_2H_5-C_{18}H_{37}$ is greater than that for PIC with $C_2H_5-C_{15}H_{31}$.

In order to study the nonlinear optical properties, films were prepared from dye solutions with a concentration of $\approx 10^{-2}$ M. At this concentration, PIC with each of the three substituents forms J-aggregates with an optical density of 0.4 to 0.5 at the J-band maximum and a J-band width given by $\Gamma \approx 200$ to 230 cm^{-1} .

The measurements of the nonlinear absorption spectrum were carried out by the Z-scan technique [11, 12]. We used a pulsed dye laser ($\tau \approx 5\text{ ns}$) with a tuning range of 575 to 595 nm. Figure 2 shows a typical dispersion curve (diamonds) of the nonlinear absorption spectrum. The typical features of this spectrum for the J-aggregates of PIC with each of the three substituents are as follows. An induced bleaching due to saturation of the absorption is observed at the spectral region corresponding to the exciton absorption band. The imaginary part of the third-order optical susceptibility reaches the value $\text{Im}\chi^{(3)} \approx -1.2 \times 10^{-5}$ esu at the maximum of the bleaching peak. The shape of the bleaching peak is asymmetric: owing to the partial overlap with the positive induced darkening peak, the red side of the bleaching peak decays about two times faster than the blue side. The induced darkening is red-shifted with respect to the bleaching maximum. The wavelength of the bleaching maximum was found to move to the high-frequency side by 35 to 50 cm^{-1} when the intensity increases from 0.6 to 3 MW/cm^2 . At the same time the contribution of the induced darkening grows by 30 to 40%.

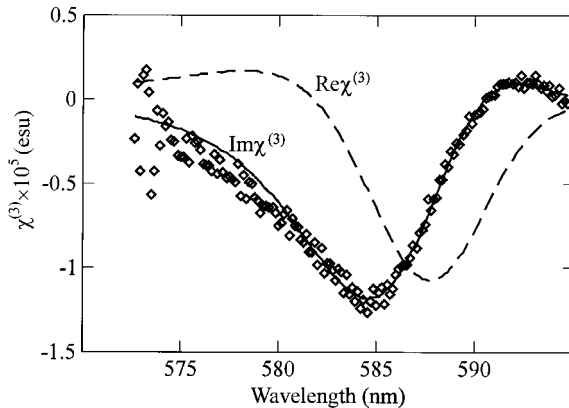


Fig. 2. Typical frequency dispersion of the third-order optical susceptibility of the J-aggregate films. Diamonds: experimental data for $\text{Im}\chi^{(3)}$; solid line: fitting curve for $\text{Im}\chi^{(3)}$ on the basis of the phenomenological four-level model; dashed line: results for $\text{Re}\chi^{(3)}$ evaluated on the basis of the four-level model [11]

Discussion Before turning to a microscopic explanation of the observed nonlinear absorption spectrum, we first analyze it in terms of a phenomenological four-level model [11]. This model mainly serves to determine the frequencies and the widths of the two (exciton) transitions underlying the partially overlapping bleaching and induced darkening peaks. Although the physics of this four-level model plays no role later on, it may be thought of to consist of two two-level subsystems with their frequencies close to each other. The first subsystem contains the ground state and the state at the bottom of the one-exciton band. The effect of saturation of the absorption in this subsystem causes the induced bleaching of the J-band. The one-exciton state, corresponding to the upper state of the first two-level subsystem, relaxes both to the ground state and to the lower state of the second two-level subsystem. A subsequent absorption of light in the second subsystem then gives rise to the induced darkening.

A fit of the experimental data using this four-level model is presented by the solid line in Fig. 2. This fit yields the characteristics of the two transitions that are relevant to the spectrum: The transition responsible for the bleaching peak has a wavelength of $\lambda_1 \approx 585$ nm, while the transition responsible for the induced darkening is red-shifted relative to this bleaching transition by $\Delta\omega \approx -(130 \text{ to } 160) \text{ cm}^{-1}$ (the minus sign indicates a red-shift). The width of the darkening transition is $\Gamma_2 \approx 140 \text{ to } 180 \text{ cm}^{-1}$.

Ideally, the wavelength λ_1 and width Γ_1 corresponding to the first two-level subsystem should be equal to those obtained from the linear absorption spectrum. This coincidence is indeed observed for the J-aggregates of PIC with the substituent $\text{C}_2\text{H}_5\text{-C}_{10}\text{H}_{21}$, where the width of the bleached transition obtained from our fit is $\Gamma_1 \approx 200 \text{ to } 220 \text{ cm}^{-1}$. On the other hand, for the J-aggregates with the substituents $\text{C}_2\text{H}_5\text{-C}_{15}\text{H}_{31}$ and $\text{C}_2\text{H}_5\text{-C}_{18}\text{H}_{37}$, the width calculated from the nonlinear absorption spectrum turns out to be narrower by 10 to 15% ($\Gamma_1 \approx 175 \text{ to } 200 \text{ cm}^{-1}$) in comparison to the width obtained from the linear absorption spectrum. At this moment, we have no explanation for this extra nonlinear narrowing.

Finally, we have used the four-level model with the obtained fit parameters to calculate the spectral shape of the real part of the third-order nonlinear optical susceptibility (dashed line in Fig. 2) [11].

We now turn to a more microscopic explanation of the observed nonlinear absorption spectrum, based on a Frenkel exciton model. From pump-probe experiments it is well-known that J-aggregates generally exhibit an induced darkening peak that is *blue-*

shifted with respect to the J-band [13]. Within a model of noninteracting one-dimensional Frenkel excitons, this blue-shifted induced darkening results from the transition from the bottom of the one-exciton band to the bottom of the two-exciton band (effective three-level system) [13 to 15]. This model of noninteracting excitons cannot explain the *red*-shifted induced darkening observed in our experiments. However, as was pointed out in Ref. [16], a strong negative exciton–exciton interaction would give rise to a red-shifted darkening in J-aggregates. This red-shifted peak results from optical transitions from the bottom of the one-exciton band to a biexciton state, which arises below the two-exciton band due to bound exciton pairs.

It is to be noted that a red-shifted nonlinear darkening was also observed in [6]. In this work the decrease of the nonlinear darkening frequency was attributed to transitions from states inside the one-exciton band, which are populated by exciton–phonon coupling. Exciton–exciton interactions were not invoked in this explanation. Also pump–probe experiments with picosecond light pulse of high intensity showed some spectral features that were qualitatively similar to those observed in our experiments [17], namely the appearance of a red-shifted induced darkening and a bleaching maximum moving to the high-frequency side with increasing intensity of the incident light. These features were attributed to the effects of exciton–exciton annihilation and biexciton formation.

If we assume that the spectral features observed by us are indeed caused by a strong exciton–exciton interaction and we use the data obtained from the above four-level system analysis, we can estimate the strength A of the nearest-neighbor exciton–exciton interaction (see Ref. [16] for the model Hamiltonian used). As was shown by Spano [16], exciton–exciton interactions only cause a red-shifted induced darkening if $A < 0$ while $|A| > 2|J|$. Here, J is the usual excitation transfer interaction strength between nearest neighbors. In fact, within the interacting exciton model, the difference $\Delta\omega$ between the resonance frequencies corresponding to the biexciton induced darkening peak and the one-exciton bleaching peak reads [16]:

$$\Delta\omega = \frac{1}{\hbar} (4J(J/A - 1) + A). \quad (1)$$

From our experiments, we have $\Delta\omega = 130$ to 160 cm^{-1} (see above) and $J \approx -550 \text{ cm}^{-1}$ (from the red-shift of the J-band relative to the monomer transition). Substituting these numbers into Eq. (1), we arrive at $A \approx 2.8$ to $2.9J$. Here, it is to be stressed that A is, like J , indeed negative, as is necessary to obtain a red-shifted biexciton. Furthermore, the obtained value for A indeed meets the criterion $A > 2|J|$ to form a biexciton at all. In fact, Eq. (1) also gives a second solution for A , which does not meet the latter criterion and should, therefore, be discarded.

We finally address the change in the permanent dipole moment $\Delta\mu_p$ of a single PIC molecule upon its excitation. We may estimate $\Delta\mu_p$ from the obtained value for A , since (assuming dipole–dipole interactions) the latter may be expressed as

$$A = (\Delta\mu_p^2/a^3) (1 - 3 \cos^2\theta_p). \quad (2)$$

Here, a is the distance between nearest-neighbor PIC molecules and θ_p is the angle which $\Delta\mu_p$ makes with the aggregate axis. In general, θ_p differs from the angle between the transition dipole moment and the aggregate axis. Using the value $a = 4.5 \text{ \AA}$ and $\theta_p = 0$ we arrive at $\Delta\mu_p \approx (3.7 \text{ to } 3.8 \text{ D})$, which corresponds to (35 to 45)% of the transi-

tion dipole moment (≈ 8.2 D as calculated from experimental data obtained in [3]; ≈ 10 D according to [18]). The value $\theta_p = 0$ was used to obtain a lower limit to $\Delta\mu_p$. The thus obtained value for $\Delta\mu_p$ is three to four times larger than the value reported in [19]. Finally, we note that the angle of the transition dipole with the aggregate axis is close to the magic angle (54.7° [20]), which explains that J is smaller than A in spite of the fact that the transition dipole is larger than our (lower) estimate of the permanent dipole change.

Conclusion Films of J-aggregates of PIC iodide with several N-alkyl substituents were obtained. These films were shown to possess a giant third-order optical susceptibility ($|\chi^{(3)}| \approx 10^{-5}$ esu) at the exciton absorption band. The saturated absorption peak (bleaching) was found to be narrowed relative to the one-exciton transition (the J-band) for J-aggregates of PIC with the substituents $C_2H_5-C_{15}H_{31}$ and $C_2H_5-C_{18}H_{37}$, while for the substituent $C_2H_5-C_{10}H_{21}$ this narrowing was not observed. We have interpreted the nonlinear absorption spectrum, in particular the observed red-shifted induced darkening, in terms of a Frenkel exciton model with exciton-exciton interactions. The latter have a strength $A \approx -1600$ cm $^{-1}$, which indicates a change in the molecular permanent dipole upon excitation of at least 3.8 D.

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